

# COATINGS. ENAMELS

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## DEVELOPMENT OF AN UNDERCOAT LAYER FOR DENTAL PORCELAIN

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Composites are developed on the basis of feldspar and hydroxyapatite with fluorite additives suitable for making ceramic coating for dental prostheses with good camouflaging properties and shape stability. The mechanism of the coating formation and their physicochemical properties are investigated.

Metal ceramics used in stomatology combines all the advantages of such materials as metal and porcelain. Initial materials for making dental porcelain are various oxide materials, including natural silicates, such as feldspar, quartz, and kaolinite. Additives providing for adhesion of the undercoat layer to metal and imparting strength and good exterior appearance to the ceramic coatings are introduced in batch compositions. Furthermore, contemporary medical practice often uses phosphor-bearing calcium compounds as materials for implants [1]. It is expedient to investigate the properties of analogous materials, as their chemical composition is the closest to natural bone.

The main requirements for a primer layer in a porcelain coating for a metal-ceramic dental prosthesis are a substantial camouflaging effect, strength, adhesion to metal, a TCLE close to the TCLE of the metal base, chemical purity, non-toxicity, and biocompatibility [2].

The main reason for dental coating defects is insufficient adhesion of the ceramic layer to the metal. The strength of the adhesion of the ceramic to the metal depends on the development of chemical, mechanical, and diffusion bonds at the contact boundary. To ensure strong adhesion by means of physical adsorption and formation of chemical (valent and covalent) bonds, materials need to satisfy stringent requirements. Furthermore, the strength of bond of a ceramic layer to metal depends on the oxide film thickness at the phase boundary, the heating rate in firing, the cooling rate, the quantity of pores, and residual stresses [3]. All the listed properties obviously depend on the phase and chemical compositions of composites, including the anion component of salts introduced.

Studies were performed on the basis of a composition proposed by us that is indicated by a figurative point on the

$K_2O - SiO_2 - Al_2O_3$  phase diagram (Fig. 1). The composition has an elevated TCLE equal to  $12.05 \times 10^{-6} K^{-1}$  (for reference, the TCLE of cobalt-chromium melt is  $12.59 \times 10^{-6} K^{-1}$ ).

The point of the composition selected for our study is slightly below the range outlined by the dashed line indicating dental mixtures traditionally used in international practice [Super Porcelain AAA (Japan), Vita WMK-68 (Germany), 3M (U.S.), etc.]. Such selection guarantees a decreased amount of cristobalite formed in the decomposition of orthoclase, which, in turn, decreases the risk of crackle in cooling of the metal-ceramic composite. Glasses of the  $K_2O - Al_2O_3 - SiO_2$  system have a low crystallization capacity, and the selected composition, whose figurative point is located on the boundary curve, has a stable vitreous state in the form of a solid.

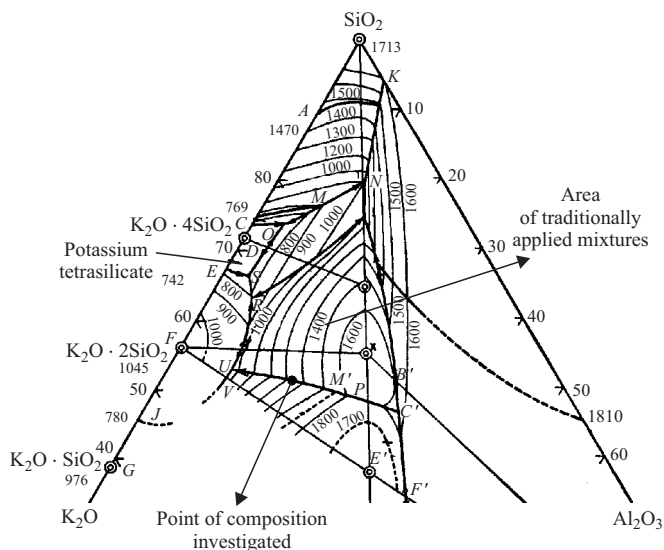


Fig. 1. A fragment of phase diagram of  $K_2O - Al_2O_3 - SiO_2$ .

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TABLE 1

Mixture	Melting point, °C	Exposure duration, min
GF1	1070	–
GF2	1150	–
GF3	1150	15
GC	1150	15

A high viscosity provides for shape stability of the melt and, accordingly, a desirable shape of the product. However, to impart higher mechanical strength and corresponding optical characteristics to a coating, it was necessary to introduce a seed-forming oxide into the mixture and to slightly decrease the melt viscosity. Accordingly, it was proposed to replace part of the glass-forming compound (silicon oxide) by a lower-melting component and to increase the ratio  $\text{Na}^+ : \text{K}^+$ . It was expected that the melt mobility would increase and, accordingly, more favorable conditions for the formation of crystalline aggregates would be provided. Replacement of a part of the potassium alkali component by sodium and lithium and a part of the glass-forming component by boron oxide lowered the batch melting point to 1150°C. Implementation of fritting at a temperature of 1200°C leads to the formation of a sufficient quantity of leucite phase seeds, which generate crystallization under subsequent heat treatment of the coating on the metal–ceramic tooth crown.

Fritting of the mixtures considered was carried out at different temperatures and different duration of exposure at a maximum temperature (Table 1). Zinc oxide and fluorides were used as crystal formers. In order to study the effect of the anion component, lithium oxide was introduced into mixture GF in the form of lithium fluoride LiF and into mixture GC in the form of lithium carbonate  $\text{Li}_2\text{CO}_3$ . All mixtures were cooled in cold water, i.e., were subjected to hardening.

Mixtures containing the fluorine ion (GF1, GF2, and GF3) after melting had a white color and were opaque and lustrous. The mixture GC containing the carbonate ion was clear as glass. Intense gas emission was observed in melting the latter mixture.

According to the x-ray phase analysis data, mixtures GF were mainly represented by a phase resembling metastable nepheline. Leucite peaks are weakly expressed, as well as peaks of orthoclase. The presence of a phase of the type of metastable nepheline indicates that silicon oxide is bonded in sodium silicates. Free quartz and cristobalite are not registered. The systems in general are amorphous and have several weakly expressed crystalline phase peaks. As fritting temperature and exposure duration increases, the intensity of orthoclase and leucite peaks decreases, whereas metastable nepheline peaks do not change, and the system becomes more amorphous. This is evidence of a decrease in the amount of orthoclase and leucite due to their decomposition and dissolution in the vitreous phase.

The glass GC is more amorphous and weakly crystallized and has several peaks. The main crystalline phases are

TABLE 2

Sample	Main shrinkage, %	Water absorption, %	Microhardness, MPa	Bending strength, MPa
GF1	6	0.9	789	22.8
GF2	7	0.6	1146	33.5
GF3	5	1.0	770	29.0
GC	6	4.5	1731	40.1
GF1.5	5	0.5	4736	36.1
GF1.10	6	0.5	5028	40.0

leucite and orthoclase. Nepheline is weakly represented. Quartz and cristobalite are not identified. The batch GC containing  $\text{Li}_2\text{CO}_3$  and the product of its fritting is mainly represented by a vitreous phase, in contrast to batch GF containing LiF, which is due to the absence of a crystallization effect determined by fluorine ions.

The principal distinction of crystalline phases containing different lithium salts is the fact that the mobile low-viscosity melt with  $\text{LiCO}_3$  crystallizes, forming leucite, and the more viscous melt containing LiF under abrupt cooling forms only a metastable phase of the nepheline type.

Samples of frit powers molded as tablets 10 mm in diameter and 2–5 mm high and rods of size  $55 \times 6 \times 4$  mm were investigated. Tin oxide  $\text{SnO}_2$  was introduced as an opacifier into GF1 in an amount of 5% (mixture GF1.5) and 10% (mixture GF1.10). The molded samples were fired at a temperature of 900°C with an exposure at the final temperature of 30 min. The main properties of the samples are listed in Table 2.

Shrinkage of all samples is virtually equal. The water absorption of all mixtures GF fritted in different conditions does not change significantly and is quite acceptable for dental mixtures. The water absorption of mixture GC is significantly higher, which points to increased open porosity; however, this is quite admissible for a primer layer.

The bending strength of samples of mixture GF is different. The higher the fritting temperature, the stronger the sample. The highest strength values are registered in samples of mixtures GC and GF1.5 and GF1.10 containing tin oxide. The increased strength is due to the existence of a reinforcing crystalline phase: leucite in mixture GC and tin oxide in mixtures GF1.5 and GF1.10.

The TCLE was measured in all mixtures (Table 3). For reference purposes the TCLE of cobalt-chromium steel (KKhS) is indicated in Table 3.

With increasing fritting temperature and exposure duration, the TCLE of the mixtures grows. On introducing tin oxide, the TCLE insignificantly decreases, which makes it possible to use this opacifier. The TCLE of mixture GC is significantly higher than that of mixture GF under similar fritting conditions.

The effect of introducing tin oxide into prepared frit on the properties of mixtures GF and GC during its decomposition of a steel (KKhS) dental crown was investigated. Firing was implemented in a vacuum furnace at a temperature of

TABLE 3

Temperature interval, °C	TCLE of undercoat layer, $10^{-6} \text{ K}^{-1}$						
	GF1	GF2	GF3	GC	GF1.5	GF1.10	KKhS
100 – 200	6.33	4.75	6.23	10.00	6.67	6.23	13.70
200 – 300	8.81	4.89	8.90	18.66	8.16	8.64	20.30
300 – 400	9.86	9.10	10.40	19.10	11.50	10.46	14.30
400 – 500	11.70	12.86	13.34	21.60	7.40	10.75	–
500 – 600	7.33	7.27	8.50	13.10	7.58	7.86	–

970°C without exposure. On the whole, primer mixtures based on LiF have more uniform tinting compared with analogous mixtures with  $\text{Li}_2\text{CO}_3$ . This is due, on the one hand, to the low viscosity and higher mobility of the latter melt, which allows for aggregation of tin oxide particles, and, on the other hand, to the higher chemical activity of this material entering into reaction with the base under an increased temperature.

Microscope studies of the primer layer on a steel crown revealed heterogeneity of the tinting, which is probably related to insufficient powder homogeneity in the frit powder with  $\text{SnO}_2$ . Consequently, two methods of milling and mixing frit with additives were tested: manually in a mortar and in ball mill. We also investigated the method of introducing  $\text{SnO}_2$  in the batch before frit melting. For this purpose 10% tin oxide was introduced into mixture GF (mixture GFSn). In testing, mixtures prepared by different methods (introduction of  $\text{SnO}_2$  into frit in melting, mixing in a mill and in an agate mortar) did not produce significant differences in coloring density.

Mixture GFSn was prepared under abrupt and slow cooling. Moreover, 5%  $\text{SnO}_2$  and 5%  $\text{TiO}_2$  were introduced into unfired mixture (composition GFSnTi). For reference purposes, the usual mixture GF was prepared, to which  $\text{SnO}_2$  was added after melting. Mixtures of all compositions were placed into corundum crucibles and fritted at 1050°C with a 1-h exposure. Next, the crucibles with mixtures inside were subjected to abrupt cooling in cold water, except for the crucible with mixture GFSn, which was left in the furnace for slow cooling.

The x-ray phase analysis of the obtained materials showed the following.

The method of cooling of a finished mixture GFSn had virtually no effect on its phase composition. New phases did not appear. The main part of frits is amorphous, and there are several high peaks related to tin oxide. Another crystalline phase is a metastable phase of the nepheline type. Orthoclase

and leucite are weakly manifested. Quartz and cristobalite are absent. The degree of crystallization is higher in a mixture melted with  $\text{SnO}_2$  than in a mixture melted without  $\text{SnO}_2$ , since the tin oxide grain acts as a crystallization center, but no other significant difference in phase composition is registered. The intensity of x-ray reflections of proper tin oxide virtually does not depend on the method of its introduction, which points to its inertness with respect to other batch components and to the melt.

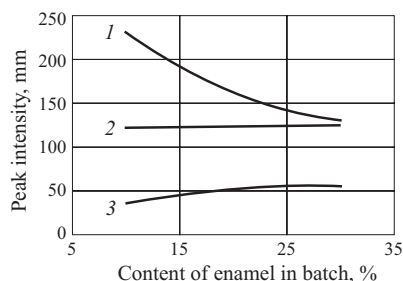
The peaks characterizing  $\text{SnO}_2$  in samples of mixtures GFSnTi are approximately half as low as in mixture GFSn, which correlates with its decreased content;  $\text{TiO}_2$  is not clearly expressed. The nepheline-type metastable phase has well-resolved peaks and other phases are weakly expressed. Quartz and cristobalite are not identified.

The effect of the method of introducing an opacifying oxide on the properties of sintered samples shaped as tablets and rods was investigated. The unit molding pressure was 40 MPa. Molded samples were fired at 900°C with a 30-min exposure. The results are shown in Table 4.

Samples GFSnTi melted at a temperature of 900°C and acquired a yellowish tint. This is related to the possibility of formation of low-melting compounds (with a melting point of 580 – 650°C) in the system  $\text{K}_2(\text{Na}_2)\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2$  [4]. The remaining samples were white, lustrous, and opaque. The microscope studies indicated that pores in samples of GF + 10%  $\text{SnO}_2$  are rounded and sized up to 100  $\mu\text{m}$ . Samples of GFSn (fast cooling) had significantly more pores than samples of the same composition under slow cooling. Samples GFSnTi have fewer pores and they are fused. Shrinkage of the sample GF containing 10%  $\text{SnO}_2$  that is introduced by different methods is virtually equal. The same refers to strength.

The TCLE of all mixtures was measured (Table 5). It is established that the method of introducing  $\text{SnO}_2$  as an

Sample	Fire shrinkage, %	Water absorption, %	Microhardness, MPa	Strength, MPa	
				bending	compressive
GFSn (abrupt cooling)	6	0.50	5033	231	31.97
GFSn (slow cooling)	5	0.05	4736	192	39.30
GF + 10% $\text{SnO}_2$ (to finished frit)	5	0.50	4397	197	39.48
Natural tooth dentine	–	–	3240	237	48.00



**Fig. 2.** Variations in peak intensity with increasing content of hydroxyapatite (1), fluorapatite (2), and leucite (3) in the batch of enamel GC.

opacifying agent does not have a significant effect on the TCLE.

On the whole, introduction of tin oxide improves not only the aesthetic properties of the coating, i.e., masks the dark-colored metal crown, but also improves its mechanical characteristics: decreases porosity and increases hardness.

To raise thermal stability and improve the masking effect, concentrated kaolinite was added into the prime coat mixture based on GF in addition to tin oxide, and part of the sodium oxide was replaced by potassium oxide to increase the melt viscosity (which, on the one hand, improves the shape stability and, on the other hand, prevents aggregation of tin oxide grains). The new composition contains (wt.%): 79 potassium feldspar, 4  $B_2O_3$ , 4 BaO, 3  $Na_2O$ , 3  $K_2O$ , 6  $Li_2O$ , and 1 ZnO and, moreover, 10  $SnO_2$  and 10 kaolinite were introduced into the finished batch above 100%.

Furthermore, the suitability of the following mixture as an undercoat layer was tested: a mixture of hydroxyapatite and fluorite in an amount from 90 to 30% was added to a ready mixture GC; the resulting composites were sintered at 1200°C with a 30-min exposure. It was found that mixtures containing over 50%  $Ca_{10}(PO_4)_6(OH)_2 + CaF_2$  do not yield a sufficient quantity of melt and are not suitable for making a dental coating and mixtures with a lower content of hydroxyapatite (GC30) satisfy the stomatological requirements (the number after GC means the weight content of  $Ca_{10}(PO_4)_6(OH)_2$  in the mixture: for instance, mixture GC30 contains 70% enamel GC and 30% mixture of hydroxyapatite and fluorite).

**TABLE 5**

Temperature interval, °C	TCLE, $10^{-6} K^{-1}$ , of samples*		
	GF + 10% $SnO_2$	GFSn (abrupt cooling)	GFSn (slow cooling)
100 – 200	6.33	5.53	5.71
200 – 300	8.64	9.31	7.71
300 – 400	10.46	10.36	11.20
400 – 500	10.75	11.60	11.46
20 – 500	7.86	7.70	8.47

\* Fritting temperature 1050°C with 30-min exposure, firing temperature 900°C with 30-min exposure.

### Properties of mixture GC30

Shrinkage, %, at temperature, °C:

900	3
1000	5
1100	10

Water absorption, %, at temperature, °C:

900	1.10
1000	0.97
1100	0.78

Microhardness, MPa, at temperature, °C:

1000	1913
1100	1507

As temperature increases, the shrinkage abruptly grows (a sample is fused and upon further heating spreads), whereas water absorption decreases gradually and insignificantly. When heated in contact with metal, composite GC30 behaves as follows (small bars 2 mm in diameter and 2 mm high were placed on a KKhS substrate and heated in a silite furnace from 20 to 1200°C; monitoring was done using an optical pyrometer):

780°C — the sample sizes decrease (sintering is registered);

950°C — fusion begins;

1050°C — fusion of all edges of the sample;

1130°C — spreading begins;

1160°C — the sample is completely spread.

It should be noted that the coating has a good masking effect.

In identifying the phase composition of mixtures containing hydroxyapatite and fluorite with enamel GC, it was found that the main crystalline phases are hydroxyapatite and fluorapatite and also the metastable nepheline phase and leucite; with increasing quantity of enamel, the intensity of leucite and fluorapatite peaks grows and the intensity of peaks  $Ca_{10}(PO_4)_6(OH)_2$  perceptibly decreases, which points to its partial dissolution in the vitreous phase (Fig. 2).

Thus, an increase in temperature and duration of exposure in melting frit based on feldspar material stabilizes the composition and properties of the material. The method of introducing the pacifying oxide does not have a significant effect on the properties of dental porcelain.

A composite based on hydroxyapatite and fluorapatite with glass (mixture GC) containing the leucite phase is suitable for making ceramic coating for dental prostheses and has good masking properties and shape stability.

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